Electron Microscopic Observation of Rod-like Micelles of Dimethyloleylamine Oxide Regenerated from Its Aqueous Solutions

Some nonionic surfactants can associate into rod-like micelles in aqueous solution, whose molecular weight is as high as 10^5 or more. Among them, hexaoxyethylene dodecyl ether (1) and hexa- and hepta-oxyethylene cetyl ethers (2–4) in water were investigated by light-scattering methods in detail. It is likely from these results that the hydrophobicity of the hydrocarbon part be strong relative to the hydrophilicity of the polar head group, in order for a nonionic surfactant to form rodlike micelles in dilute solutions.

Amine oxide is a good hydrophilic group for nonionic surfactants, and dimethyldodecylamine oxide (5, 6) and dimethyltetradecylamine oxide (5) are known to form spherical micelles in water and 0.20 *M* NaCl solutions, whose molecular weight is of the order of 2×10^4. We can expect to have rod-like micelles of nonionics with amine oxide head group, if the hydrocarbon part is made longer. In our current work on light scattering (7, 8) we have found that dimethyloleylamine oxide, $CH_3(CH_2)_7CH{=}CH(CH_2)_8N(CH_3)_2O$, forms rod-like micelles in dilute aqueous solutions.

In this work we present electron micrographs of rod-like micelles regenerated from aqueous solutions of dimethyloleylamine oxide and give a support for the results from light-scattering measurements.

Solutions of dimethyloleylamine oxide at a concentration, 0.10×10^{-2} g cm^{-3}, in water and 0.01 *M* NaCl, were prepared at 25°C, in which it was established by the analyses of light-scattering data (7, 8) that rod-like micelles having molecular weights, 890,000 and 4,760,000, respectively, are present. An aliquot of each solution was put on a carbon-coated electron microscope grid, and the specimens were negatively stained with 1% uranyl acetate solution. Photographs were taken at a numerical magnification of 50,000 with a JEM 100 C Electron Microscope, operated at 80 kV.

Figure 1 shows the electron micrographs of specimens prepared from aqueous solutions of dimethyloleylamine oxide in the absence and presence of 0.01 *M* NaCl. Tortuous thread-like images are evident in both photographs, which have a uniform and common diameter and exhibit a flexible character. They may be identified with the rod-like micelles.

The diameter of the rod-like micelles is expected to be

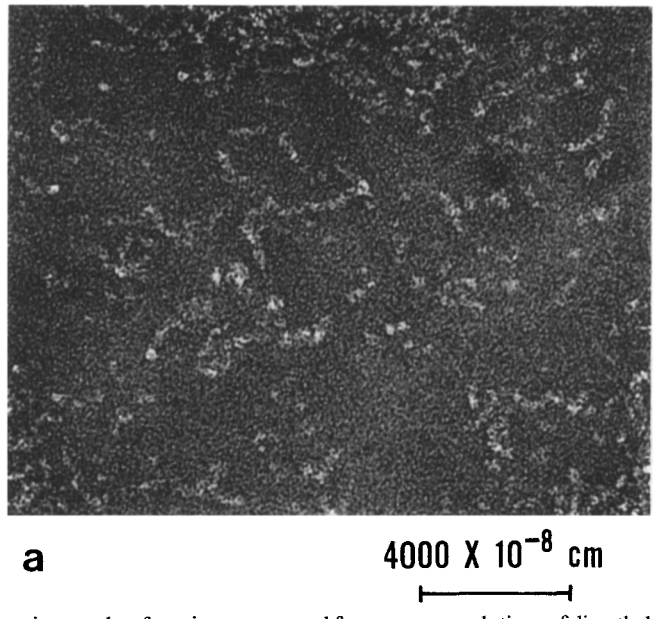

FIG. 1. Electron micrographs of specimens prepared from aqueous solutions of dimethyloleylamine oxide at concentration 0.10×10^{-2} g cm^{-3}. (a) In water, (b) in 0.01 *M* NaCl.

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FIG. 1—*Continued.*

uniformly about 60 Å, since the surfactant molecule has a length of about 30 Å. In our photographs it is as thick as 100 Å. The larger diameter of the electron micrographic images could be attributed to the collapse of micelle structure after drying.

The tortuous images observed in the photographs are in agreement with the idea of the worm-like chains for rod-like micelles (8–12). The contour lengths of the worm-like images are estimated to be 970 ± 600 and 3700 ± 1100 Å, respectively, in the absence and presence of 0.01 *M* NaCl. From the analyses of light-scattering data we have found that the contour lengths of the rod-like micelles are 740 Å in water and 3970 Å in 0.01 *M* NaCl, respectively.

Although the aggregated states of dimethyloleylamine oxide in dilute solutions could have been perturbed during the processes of electron microscopy such as staining with uranyl acetate and drying the specimens, we may conclude that the observed images of electron micrographs reflect the size and shape of rod-like micelles in solution, taking account of the good agreement between these images and the results of light-scattering studies.

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TOYOKO IMAE
RITSU KAMIYA*
SHOICHI IKEDA

Department of Chemistry and
**Institute of Molecular Biology*
Faculty of Science
Nagoya University
Chikusa, Nagoy 464, Japan

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